



2006 ALS Users Meeting Advanced Magnetic Spectroscopy Workshop
October 10, 2006
Berkeley, California



Magnetic Properties of $Ga_{1-x}Mn_xP$ Synthesized by Ion Implantation and Pulsed-Laser Melting

P.R. Stone^{1,2}

**M.A. Scarpulla^{1,2}, R. Farshchi^{1,2}, I.D. Sharp^{1,2}, J.W. Beeman², K.M. Yu²,
H. Ohldag⁴, J.D. Denlinger³, E. Arenholz³, E.E. Haller^{1,2}, O.D. Dubon^{1,2}**

¹Dept. of Materials Science & Engineering, University of California, Berkeley, CA 97420

²Lawrence Berkeley National Laboratory, Berkeley, CA 94720

³Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

⁴Stanford Synchrotron Radiation Laboratory, Menlo Park, CA 94025

Funding from DOE; NDSEG



Presentation Overview



- Introduction to Ferromagnetic Semiconductors
 - Why study $\text{Ga}_{1-x}\text{Mn}_x\text{P}$?
 - Ion Implantation Pulsed-Laser Melting (II-PLM)
- Properties of $\text{Ga}_{1-x}\text{Mn}_x\text{P}$
 - Evidence of a carrier-mediated ferromagnetic phase
 - Compositional tuning of ferromagnetic properties $\Rightarrow T_c$
 - X-ray Magnetic Circular Dichroism
- $\text{Ga}_{1-x}\text{Mn}_x\text{P}:S \Rightarrow$ The effect of compensation on ferromagnetic exchange
 - Alter magnetic properties as a function of carrier concentration
 - Effect on magnetic anisotropy
- Outlook and Conclusions



Ferromagnetic Semiconductors



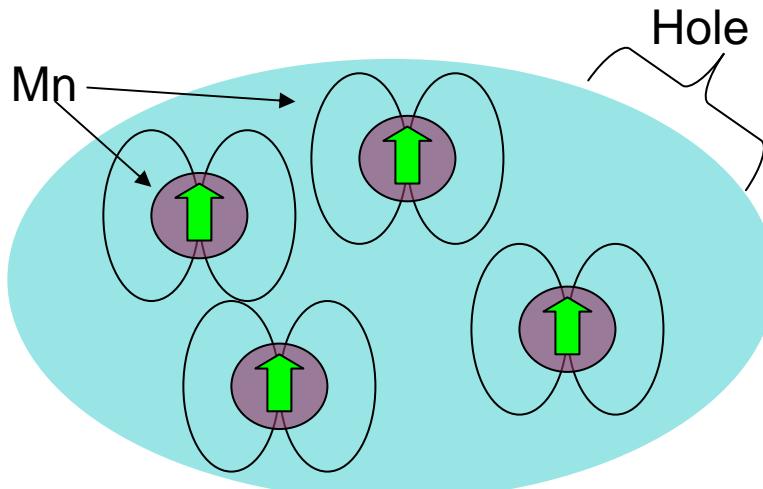
- Take advantage of both the charge and spin degrees of freedom of the electron
- Applications
 - Strong coupling transport & magnetism
 - Sources and detectors of spin-polarized currents
 - Spin-based electronics & data storage (*spintronics*)
- Strategy ⇒ heavily dope conventional semiconductor lattices with magnetically-active elements
 - Easily integrate into current technological infrastructure
 - Low solubility of magnetic elements in semiconductor lattices
 - Molecular Beam Epitaxy (MBE)
 - Ion Implantation-Pulsed Laser Melting (II-PLM)



$Ga_{1-x}Mn_xV$ Ferromagnetic Semiconductors



- $p-d$ exchange (J_{pd}) between holes & Mn_{Ga} gives ferromagnetism
- Carrier-mediated exchange $\Rightarrow T_c \propto x$ and p^m
- Substitutional Mn (Mn_{Ga})
 - Local moments
 - Provides holes \Rightarrow (e.g. 110 meV acceptor level in $Ga_{1-x}Mn_xAs$)
- Interstitial Mn (Mn_I)
 - Double electron donor
 - Forms antiferromagnetic complexes with Mn_{Ga}
- $Ga_{1-x}Mn_xAs$ is the most well-studied system
 - Zener kinetic-exchange model
 - Ferromagnetism mediated by itinerant carriers



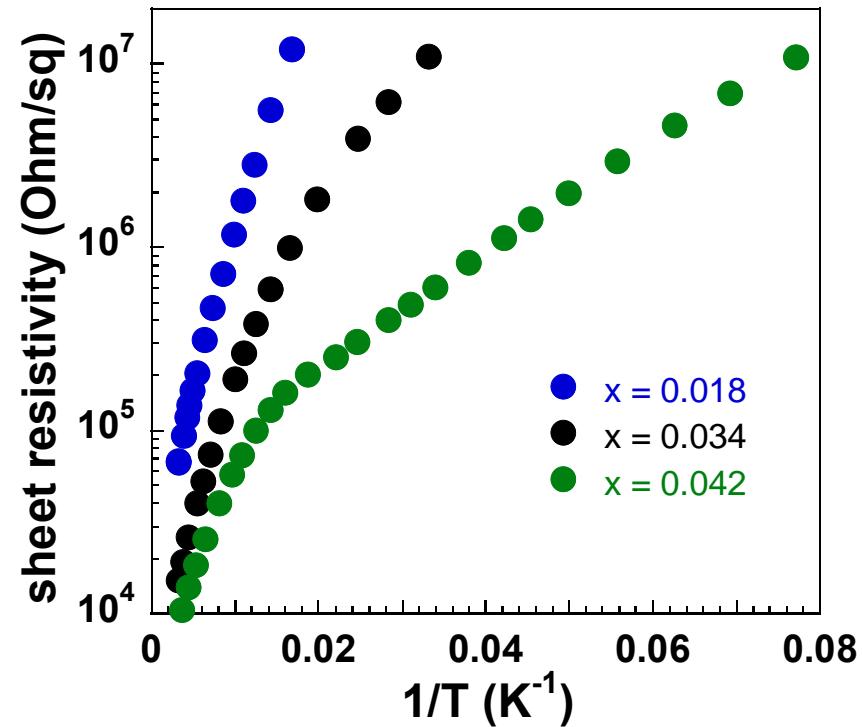
- Fundamental nature of exchange throughout Ga-Mn-pnictide series is still unclear
 \Rightarrow Important to synthesize and characterize $Ga_{1-x}Mn_xN$, $Ga_{1-x}Mn_xSb$, $Ga_{1-x}Mn_xP$



$Ga_{1-x}Mn_xP$: Effect of Anion Substitution



- Mn acceptor level is ~4 times deeper in $Ga_{1-x}Mn_xP$ than $Ga_{1-x}Mn_xAs$
 - Mn_{Ga} forms an unmerged impurity band
 - Greater hole localization
 - $Ga_{1-x}Mn_xP$ is non-metallic
 - Applies to at least $x \leq 0.042$
- Zener kinetic-exchange model may not completely describe ferromagnetism in $Ga_{1-x}Mn_xP$

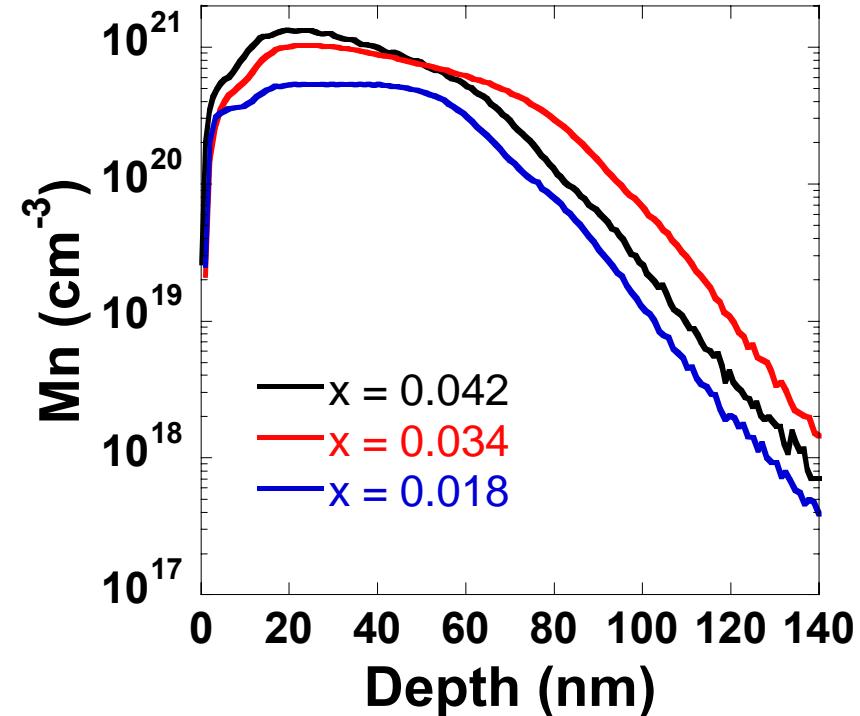
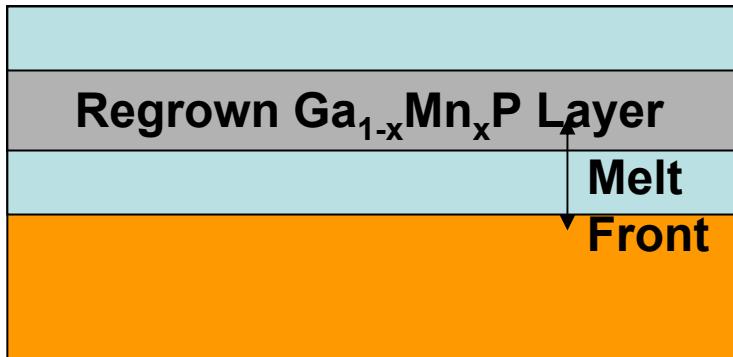




Ion Implantation – Pulsed Laser Melting (II-PLM) of $Ga_{1-x}Mn_xP$



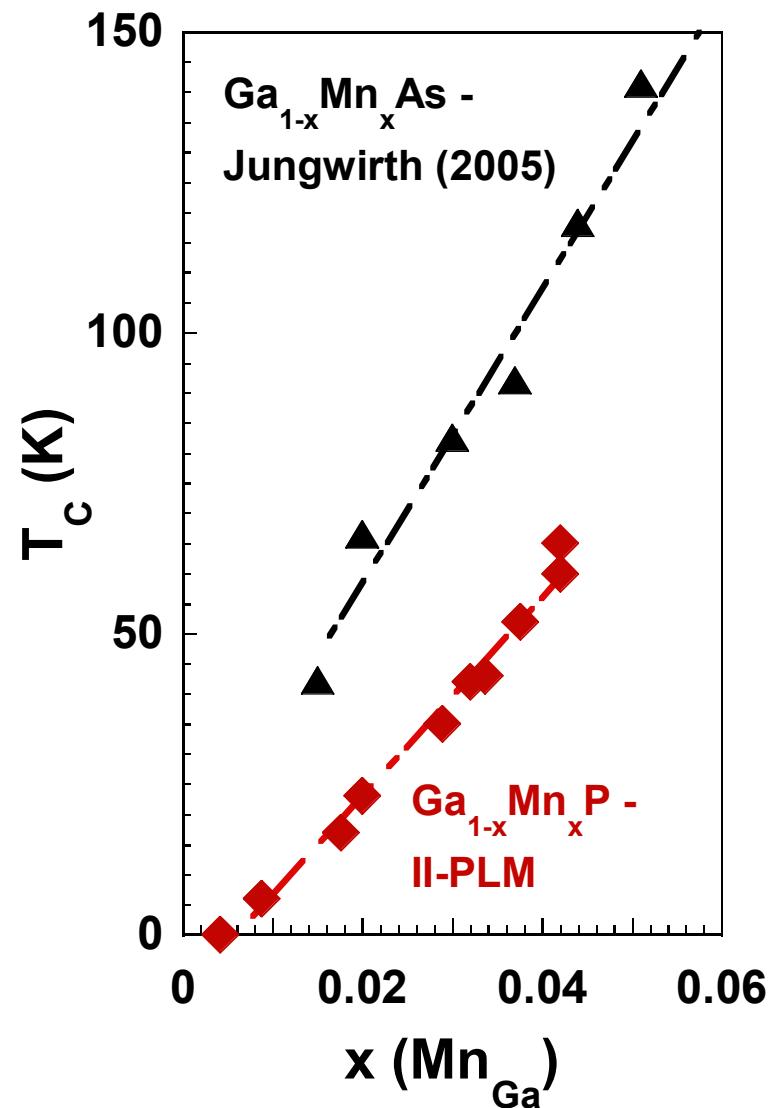
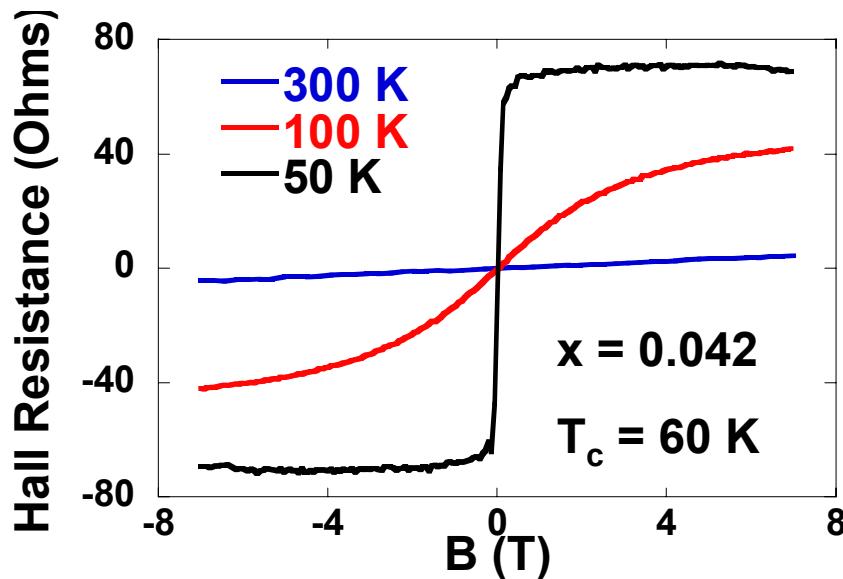
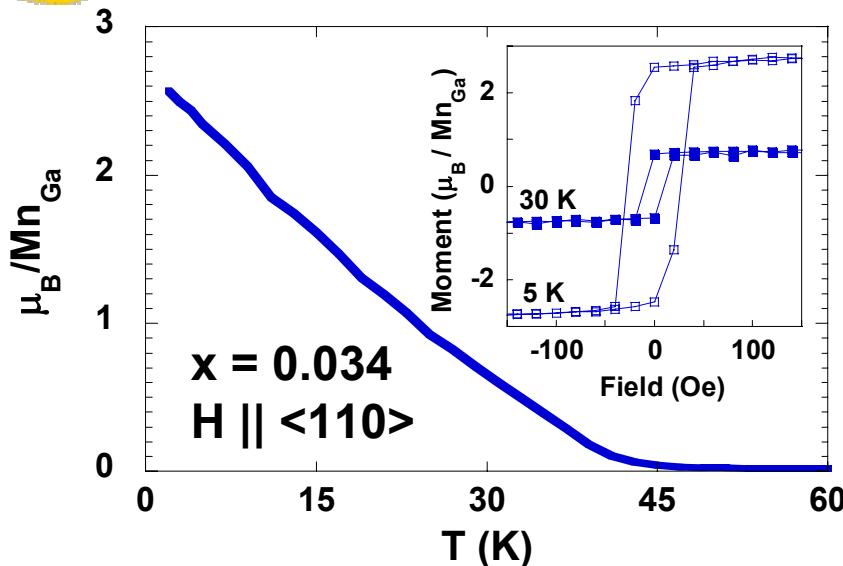
excimer laser pulse



- **Implantation:** create supersaturation in solid state
- **PLM:** repair lattice and maintain supersaturation
 - Use kinetics to overcome solubility limits
 - m/s front velocity → solute trapping
 - **x:** peak in Mn_{Ga}



Evidence of Carrier-Mediated Ferromagnetic Phase in $\text{Ga}_{1-x}\text{Mn}_x\text{P}$



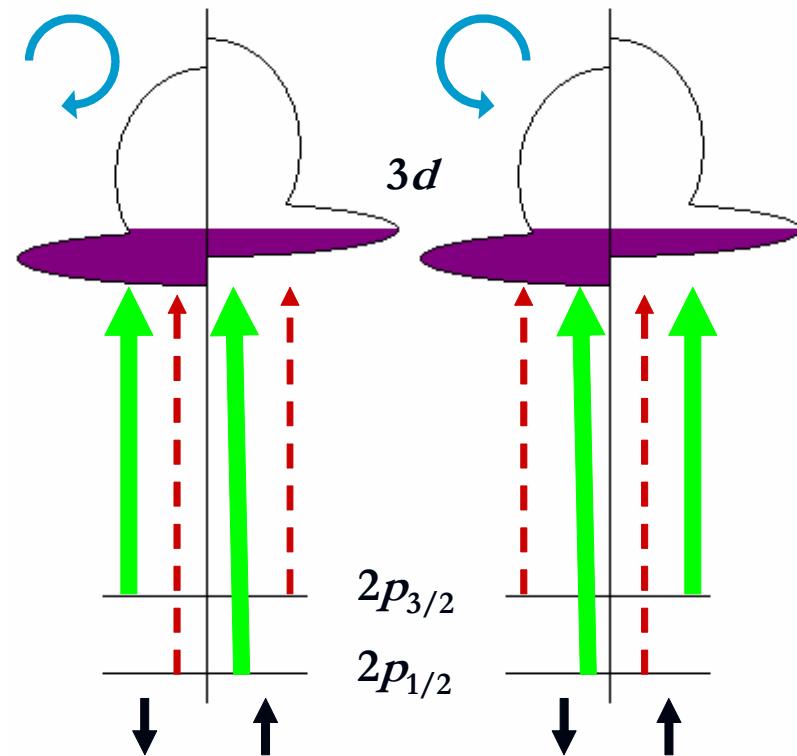
Jungwirth PRB (2005)



Mn $L_{3,2}$ XMCD of Ferromagnetic Semiconductors

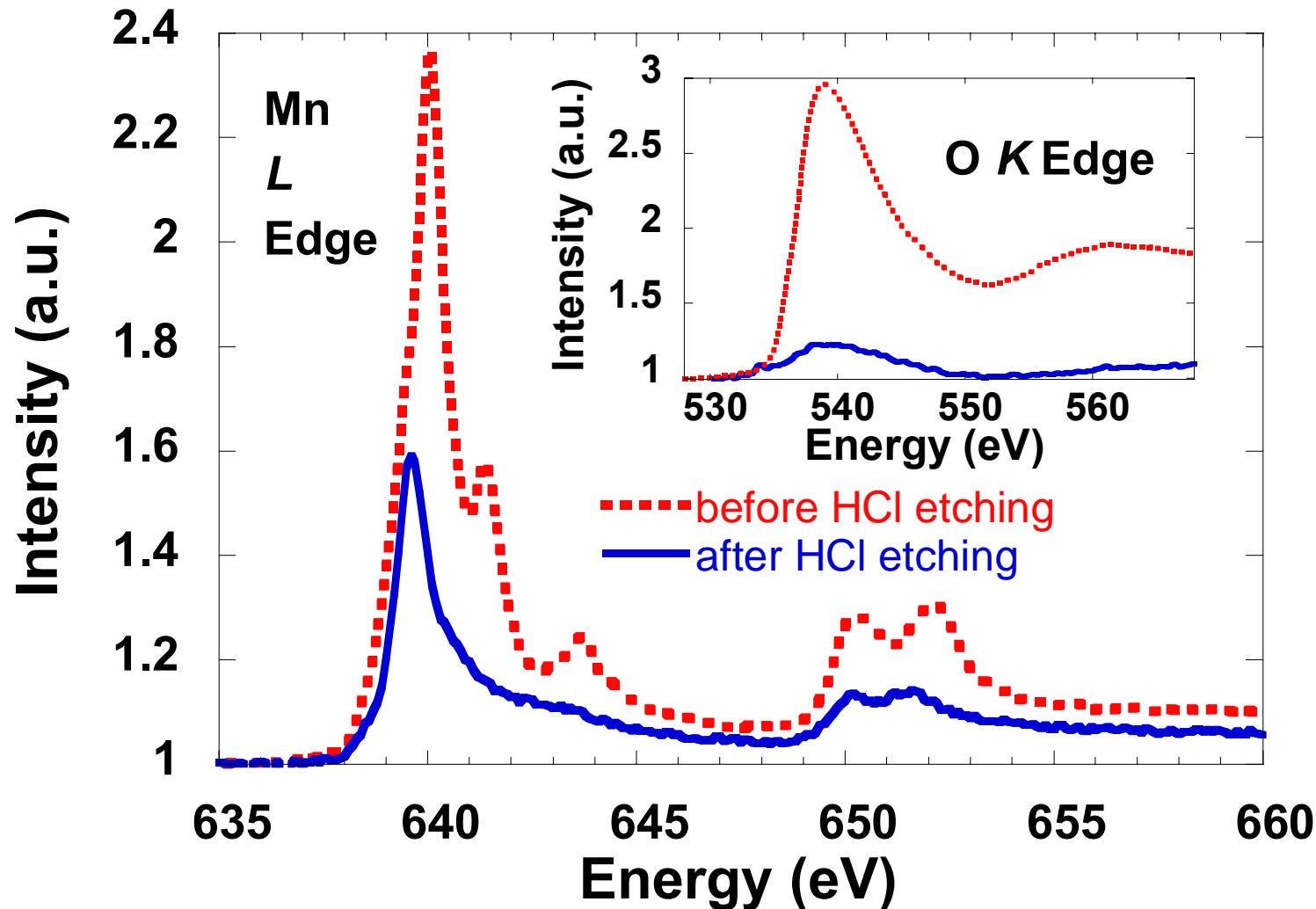


- Element specific detection of magnetism
 - Verify that Mn are magnetically active
 - Electronic nature of Mn impurity
- Apply sum rule analysis to obtain element-specific magnetic moments
 - Compare to values obtained by SQUID/RBS analysis
- XMCD in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$
 - Early studies obscured by surface oxide phases
 - Post growth HCl etch → measurement of XMCD from Mn in underlying semiconductor matrix





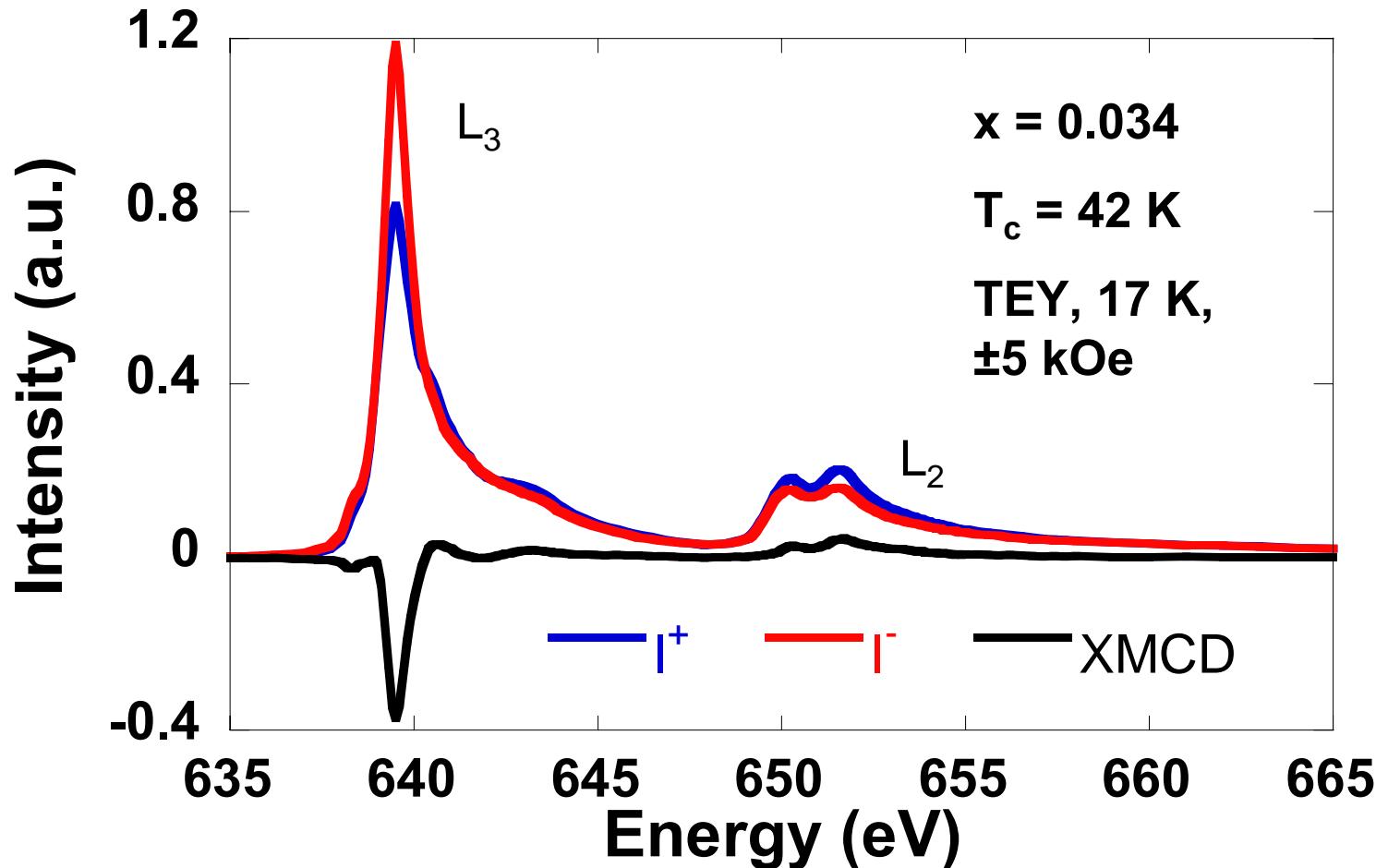
Room Temperature XAS



With J.D. Denlinger, ALS



XMCD of $Ga_{0.966}Mn_{0.034}P$



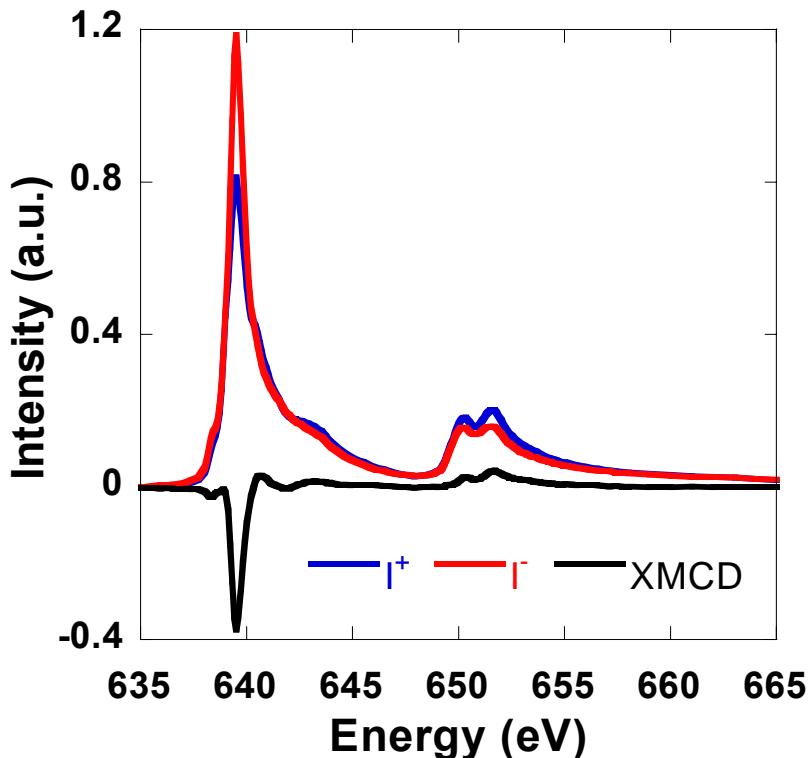
- Total Electron Yield (TEY) data collection → 3-10 nm probe depth
- Large spin polarization of 3d states at E_F



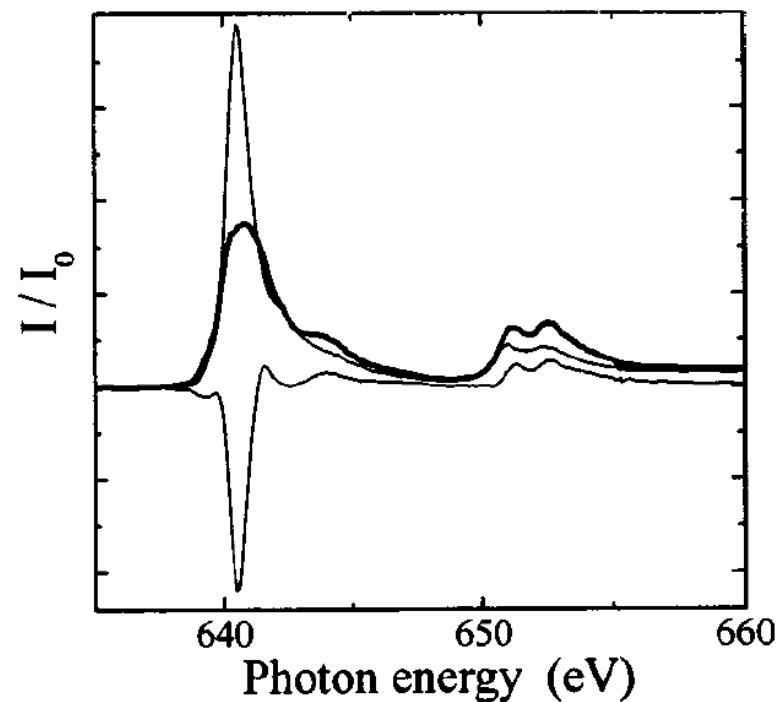
TEY XMCD Spectra of $Ga_{1-x}Mn_xP$ and $Ga_{1-x}Mn_xAs$



$Ga_{0.966}Mn_{0.034}P$ at 17 K and 5 kOe



$Ga_{0.933}Mn_{0.067}As$ at 15K and 6 kOe

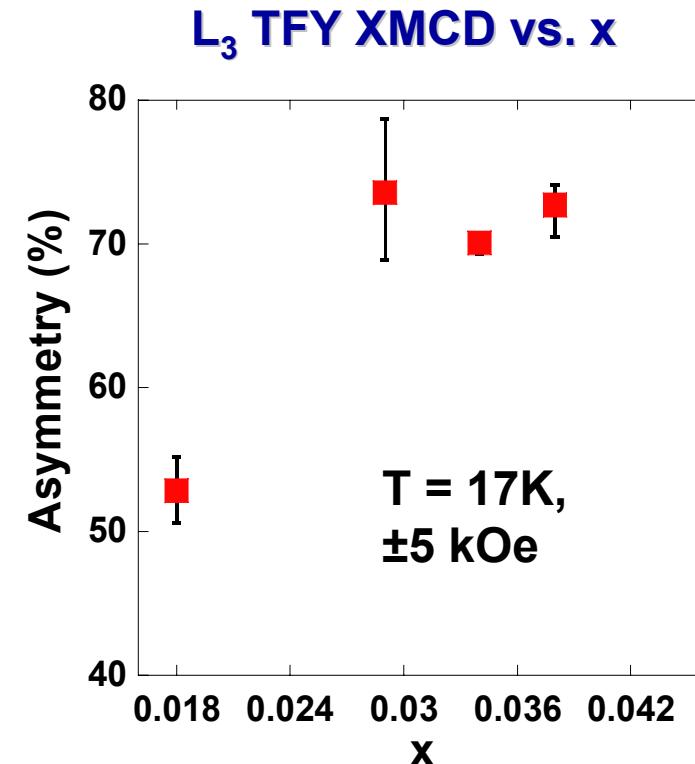
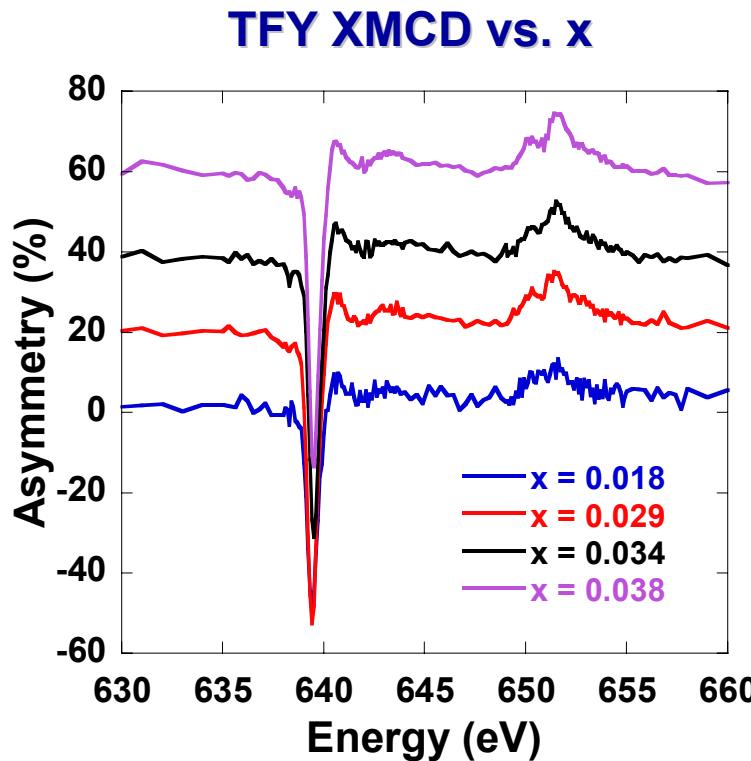


K.W. Edmonds *et al.*, Appl. Phys. Lett. **84**, 4065 (2004).

- XMCD lineshapes are indistinguishable
- Local electronic environment around Mn_{Ga} is similar in $Ga_{1-x}Mn_xP$ and $Ga_{1-x}Mn_xAs$



XMCD vs. x



- **Total Fluorescence Yield (TFY) Data Collection** → Probe depth > 10 nm
 - Better quantitative assessment of bulk film properties
- **$Ga_{1-x}Mn_xP$ asymmetry $\sim 70\%$ at L_3 for $x > 0.018$**
 - Exception at $x = 0.018 \rightarrow T_{\text{measurement}} \approx T_c$
 - **$Ga_{1-x}Mn_xAs$ $\sim 55\%$ at L_3 for $x > 0.02$**

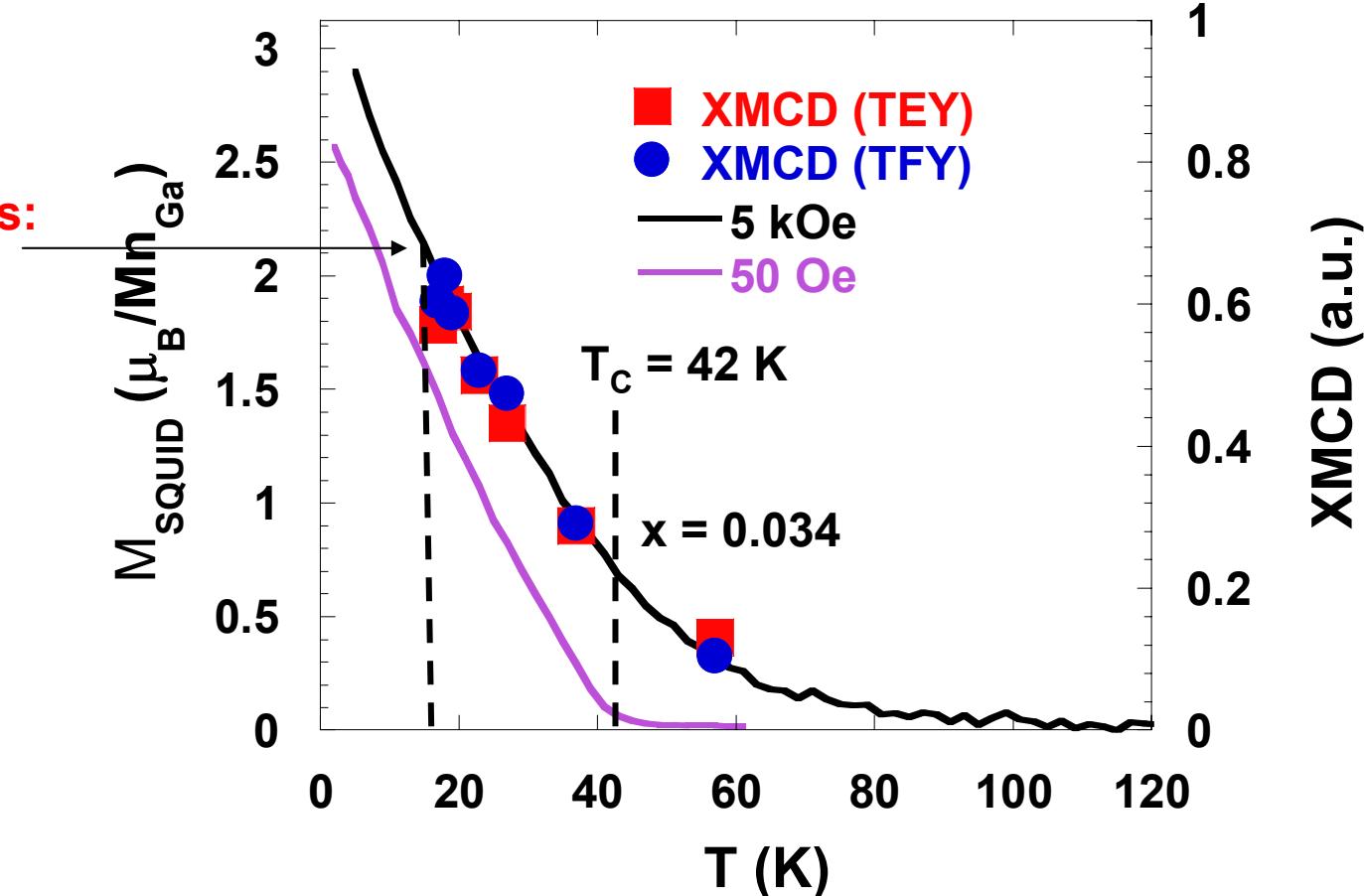


$Ga_{1-x}Mn_xP$: Surface vs. Bulk Measurements



Sum Rule Analysis:

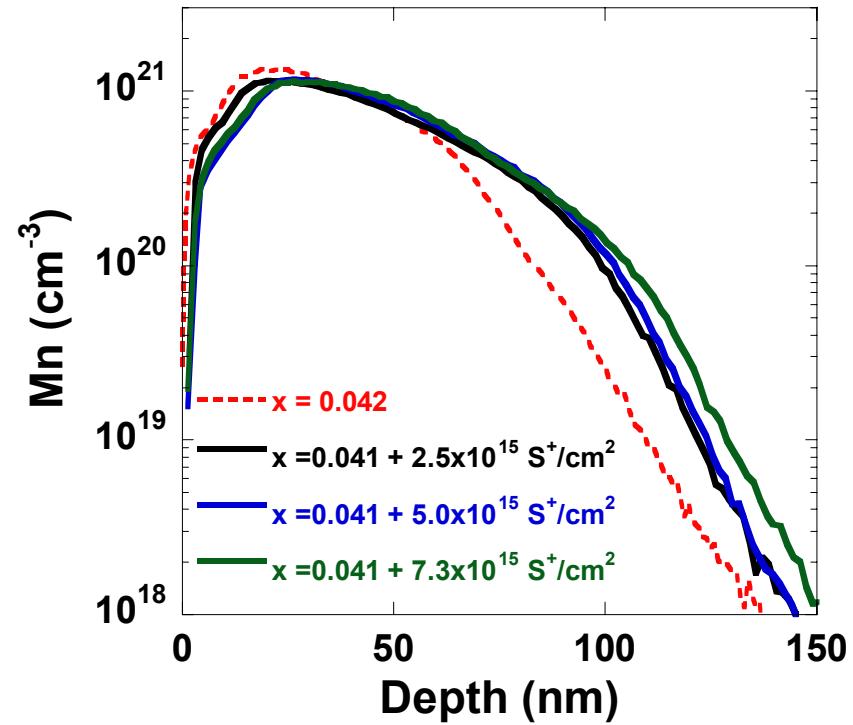
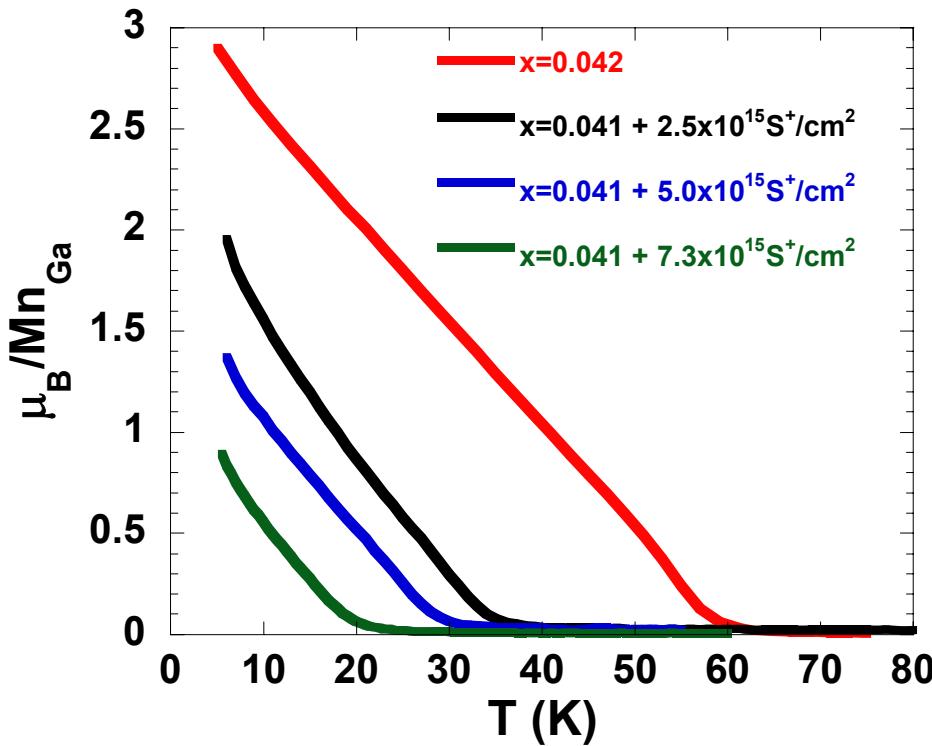
$$2.29 \pm 0.3 \mu_B/Mn_{Ga}$$



- XMCD ★ Mn magnetization
- XMCD and SQUID measure same ferromagnetic phase



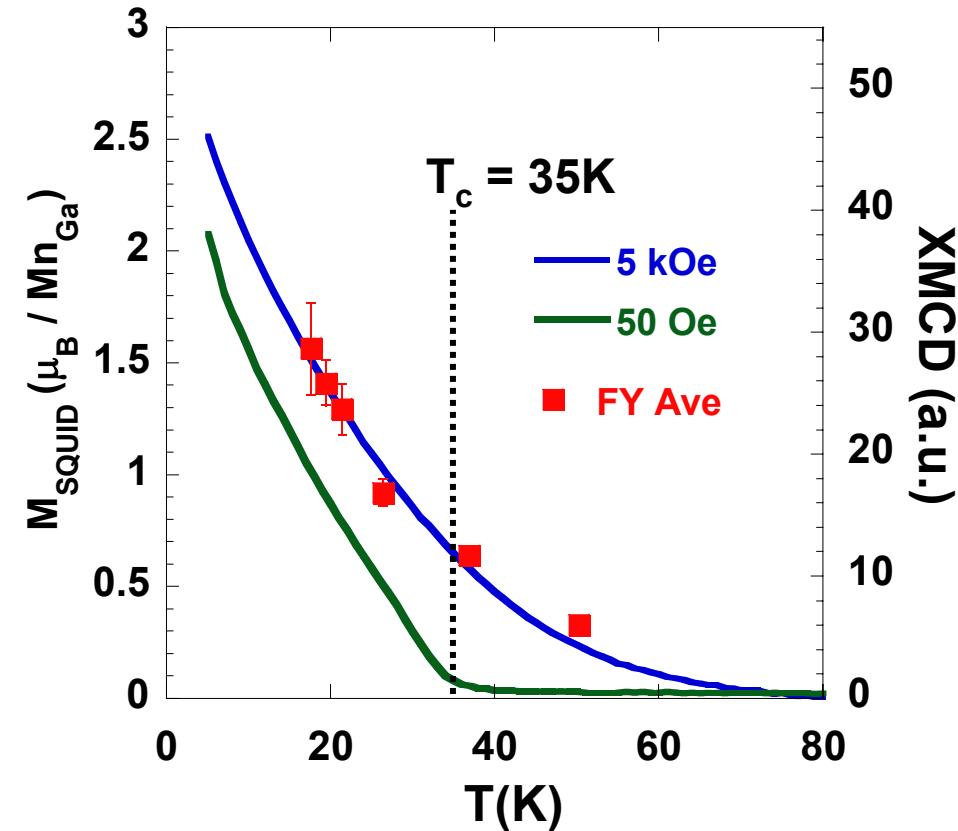
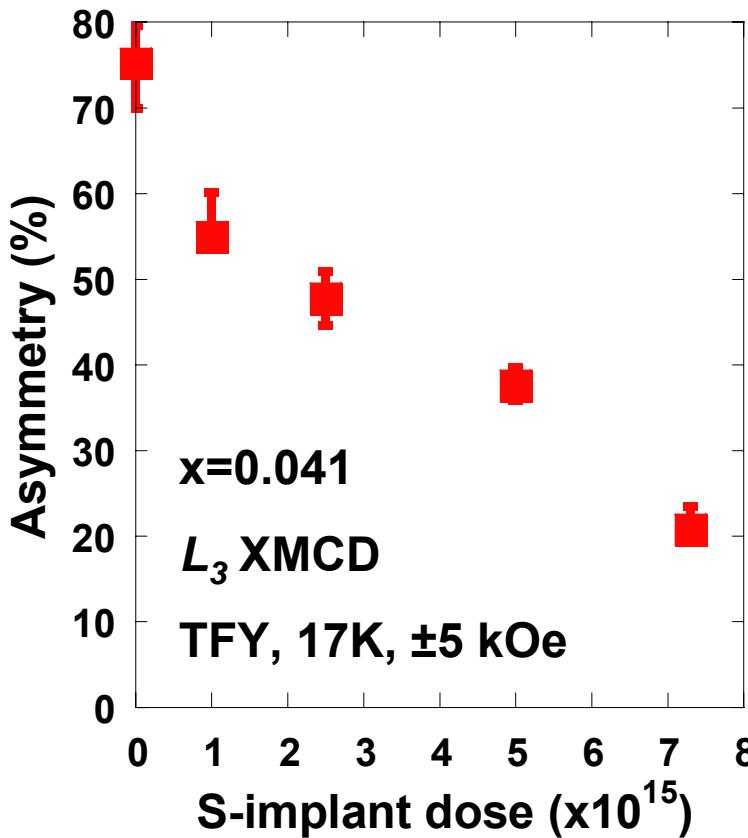
Compensation: $Ga_{1-x}Mn_xP:S$



- Carrier-mediated phase → control magnetic properties through carrier concentration
- Sulfur substitutional on a phosphorous site (S_P) is an electron donor.
 - Decrease concentration of mediating holes through sulfur codoping



Preliminary XMCD Results

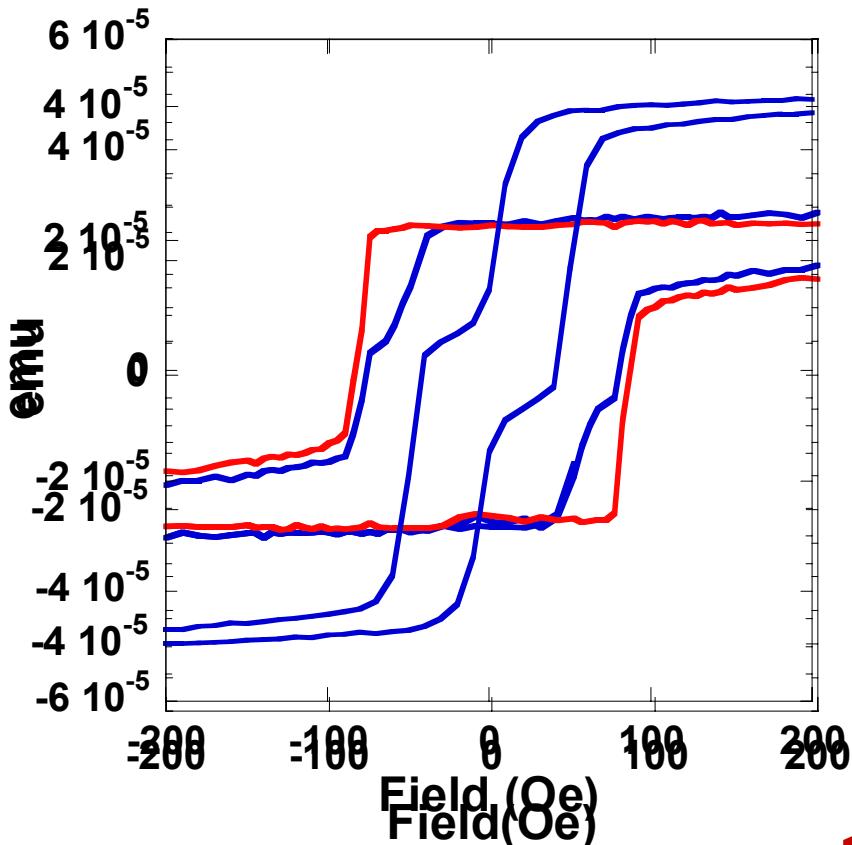


- XMCD decreases with introduction of Sulfur donors
- Inter-Mn exchange intimately related to hole concentration

$$x=0.041+2.5 \times 10^{15} S^+/cm^2$$

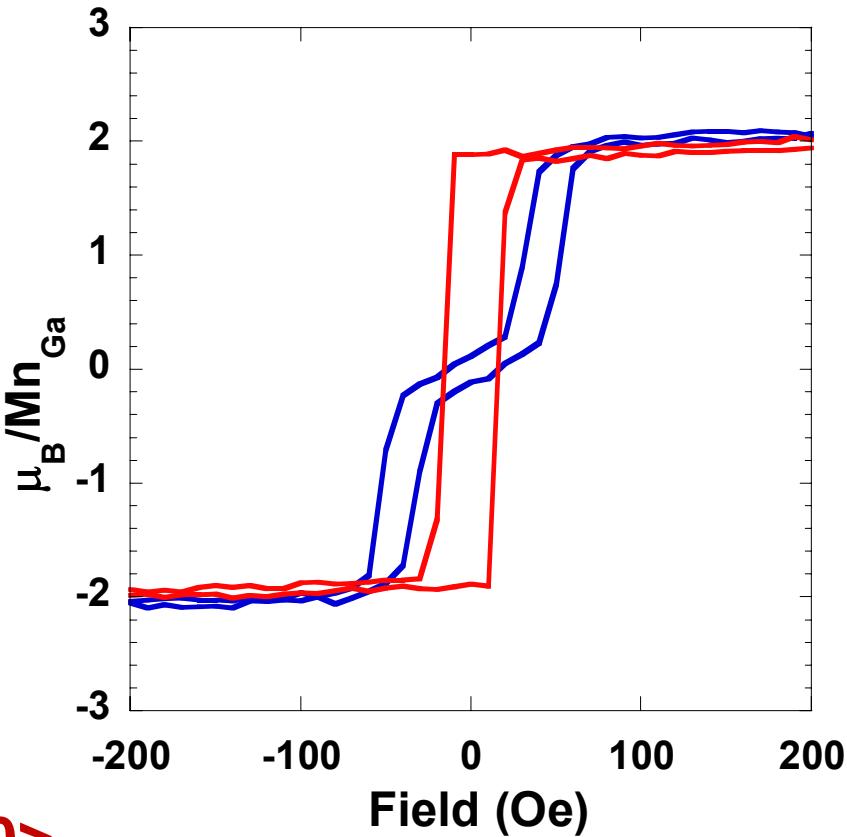


The Effect of Compensation on Magnetic Anisotropy



$\text{Ga}_{0.968}\text{Mn}_{0.032}\text{P}$

$<1\bar{1}0>$
 $<110>$



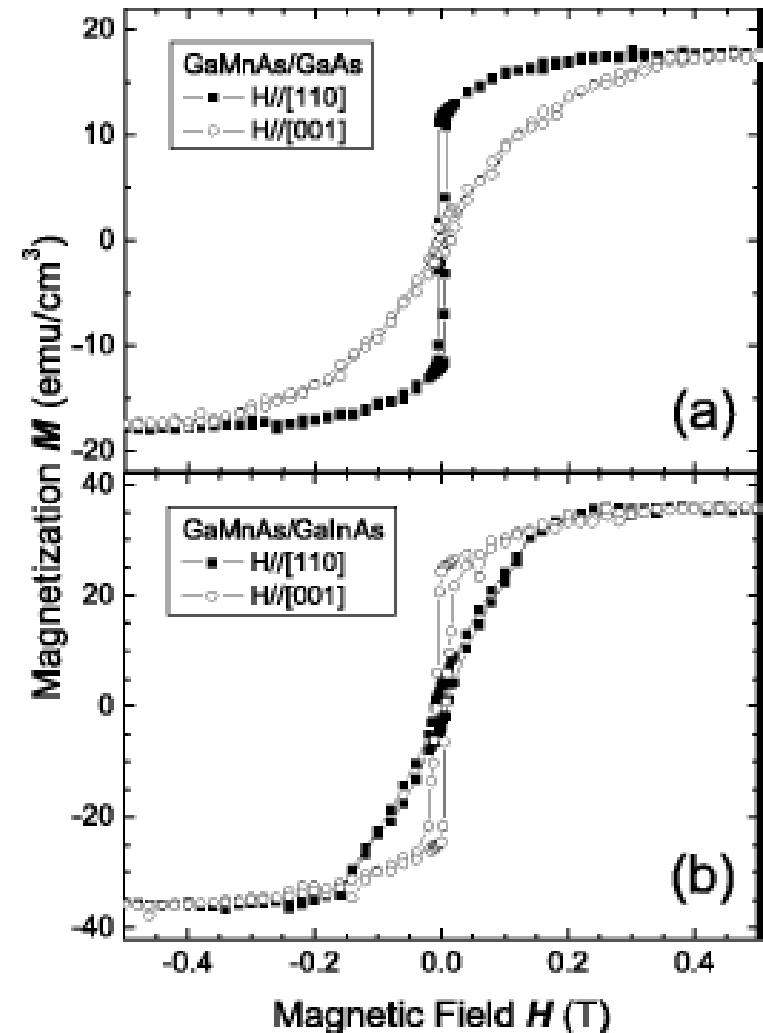
$\text{Ga}_{0.959}\text{Mn}_{0.041}\text{P} + 2.5 \times 10^{15} \text{ S}^+/\text{cm}^2$



Magnetic Anisotropy in Ferromagnetic Semiconductors



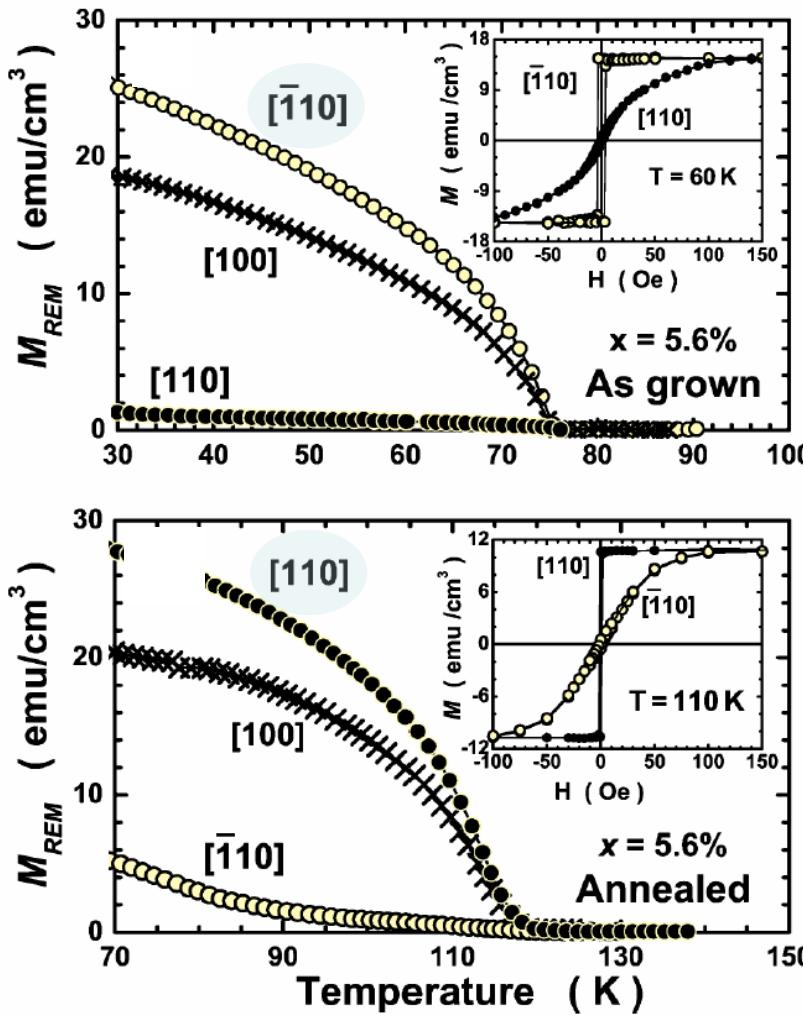
- Magnetic anisotropy → preferred orientation of magnetization vector
- Strongly dependent on:
 - Strain
 - Carrier concentration
 - Temperature
- In $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ system easy axis reorientations have been observed for each of above effects.
- Shape anisotropy is rather weak because magnetic ions are dilute
 - In $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ thin films strain anisotropy easily overcomes shape



X. Liu *et al.* PRB (2003)



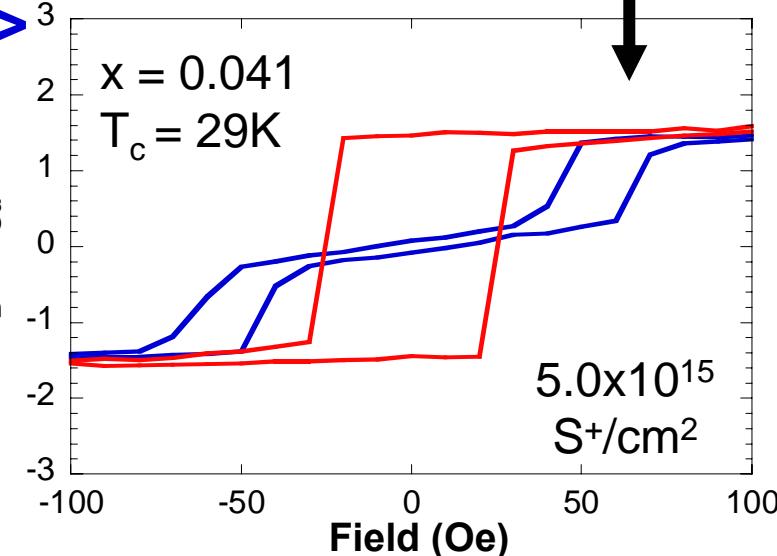
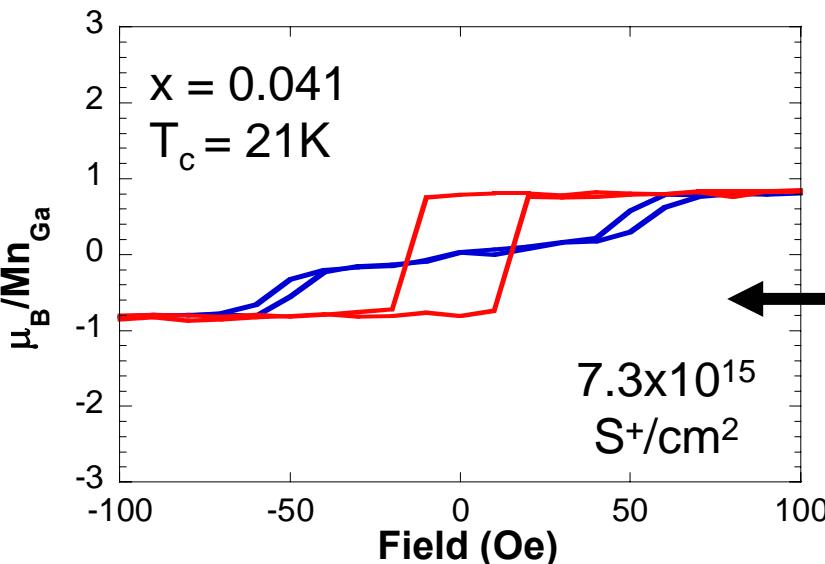
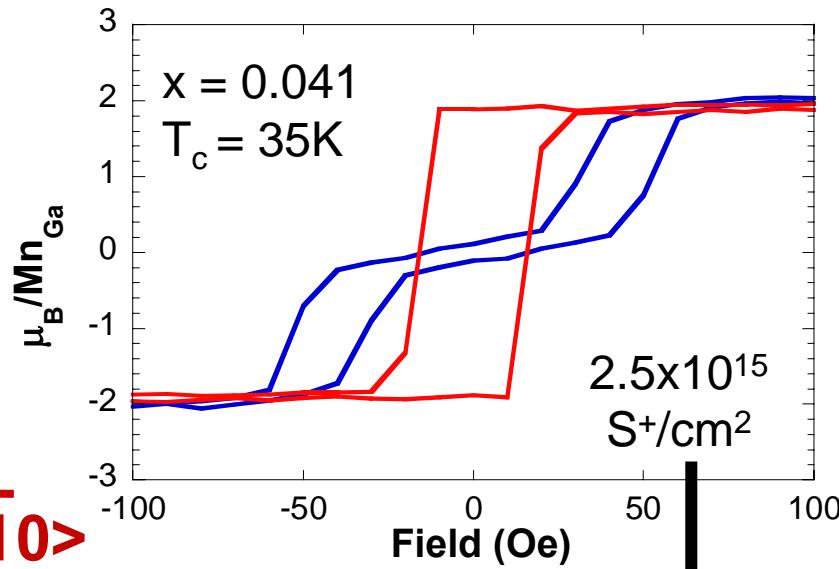
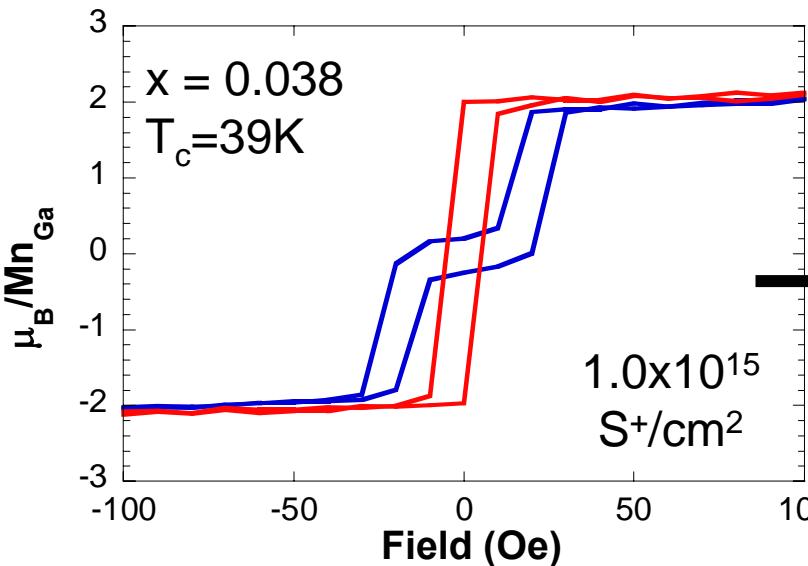
Magnetic Anisotropy in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$



- Strong in plane, uniaxial component to anisotropy
- Easy axis can be rotated from **[110]** to **[110]** by thermal annealing
 - Removes Mn_I
 - Increases hole concentration
 - Breaks Mn_{Ga}-Mn_I clusters
 - Outdiffusion of Mn_I changes strain in film
- Microscopic origin of uniaxial anisotropy is still unclear



Hole Concentration Dependent Hysteresis in $\text{Ga}_{1-x}\text{Mn}_x\text{P:S}$

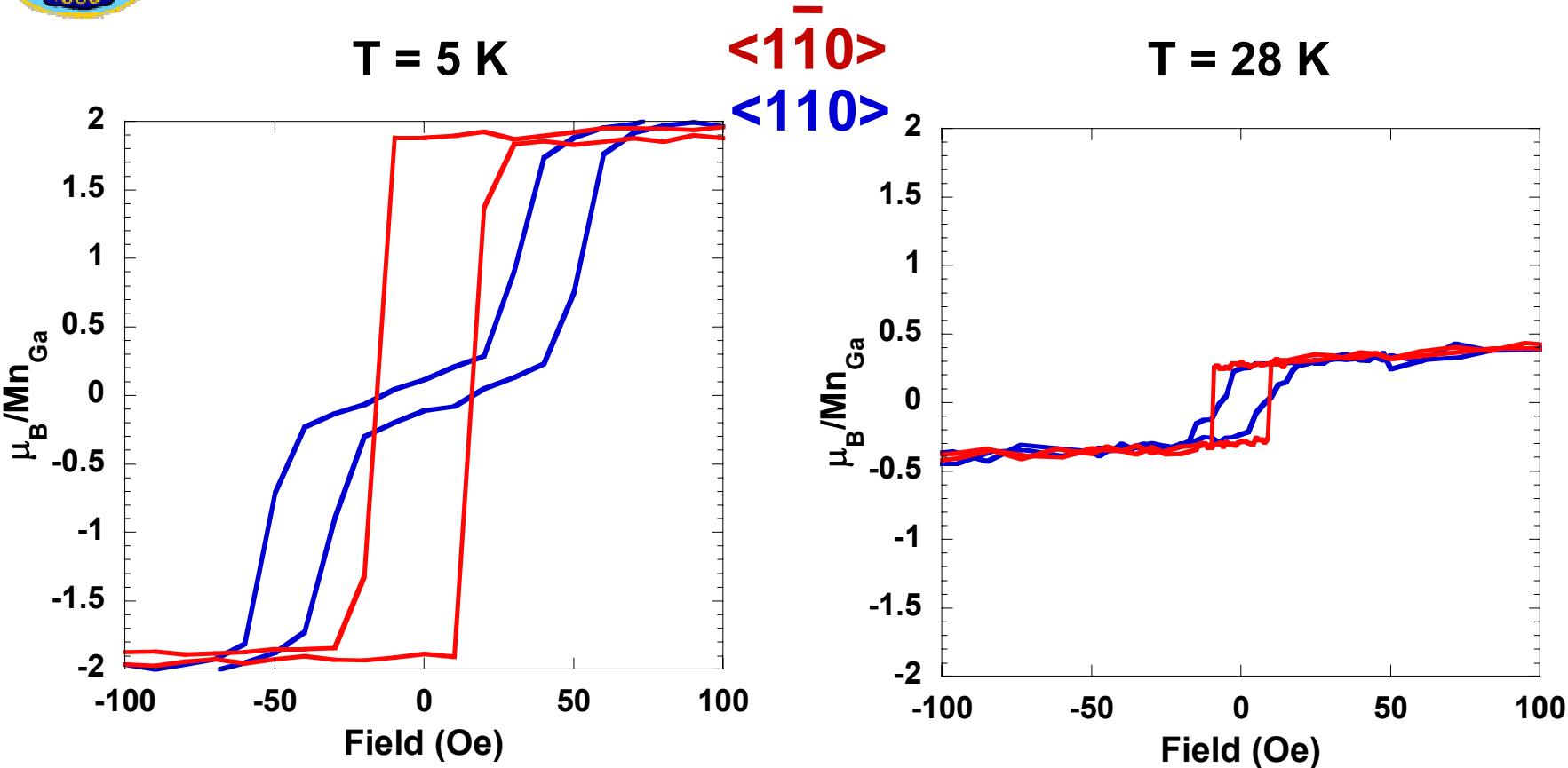


$<1\bar{1}0>$

$<110>$



Temperature Dependence of Magnetic Anisotropy



- No easy axis reorientation with temperature up to at least $T = 0.8T_c$
- Uniaxial anisotropy weakens with respect to cubic anisotropy with increasing temperature



Summary



- Synthesis of a carrier-mediated phase of $\text{Ga}_{1-x}\text{Mn}_x\text{P}$
 - Hole states have strong spin polarization from XMCD
- Compositional tuning of magnetic properties
 - Mn_{Ga} concentration (x)
 - Hole concentration (p)
- XMCD lineshapes of $\text{Ga}_{1-x}\text{Mn}_x\text{P}$ and $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ nearly identical
 - Similar Mn_{Ga} electronic environment and p-d hybridization
- Sulfur incorporation strongly affects anisotropy
 - Increase in plane uniaxial anisotropy with sulfur concentration
 - Outlook for anisotropy
 - Strain or carrier concentration?
 - Ferromagnetic resonance studies planned → Anisotropy Fields
 - Direct imaging of domain motion



Future XMCD Plans



- Continue study of $\text{Ga}_{1-x}\text{Mn}_x\text{P:S}$
 - Acquire data in TEY mode → sum rule analysis
 - Investigate anisotropy
- $\text{Ga}_{1-x}\text{Mn}_x\text{As}_{1-y}\text{Te}_y$
 - System shows compensation-driven metal-insulator transition
 - Compare to compensation effects in $\text{Ga}_{1-x}\text{Mn}_x\text{P:S}$
- $\text{Ge}_{1-x}\text{Mn}_x$
 - In collaboration with Walter Schottkey Institute
 - Group IV ferromagnetic semiconductor
 - Phase segregation
 - Mn rich clusters/precipitates depending on growth conditions
 - Mn depleted matrix